METHOD FOR MANUFACTURING Ni-Al ALLOY ANODE FOR FUEL CELLS USING NICKEL POWDERS

BACKGROUND OF THE INVENTION

Field of the invention

The present invention relates to a method for manufacturing Ni-Al alloy anode for fuel cells, more particularly to a method for manufacturing Ni-Al alloy anode for fuel cells, in which, using nickel powders, Ni powders are mixed with Ni-Al alloy powders, which are hardly sintered in themselves, to assist a sintering of Ni-Al alloy, whereby Ni-Al alloy anode can be manufactured simply, economically and compatibly with mass production even by a conventional manufacturing process for an electrode.

Generally known in the art, fuel cells are a generator directly transforming chemical energy fuel has into electric energy. Fuel cells are classified into various kinds of fuel cells including Molten Carbonate Fuel Cell (MCFC), Polymer Electrolyte Membrane Fuel Cell (PEMFC), Solid Oxide Fuel Cell (SOFC) and the like. MCFC is a fuel cell using molten carbonate as an electrolyte and consists of the key spare parts of a cathode, an electrolyte and supporter, and an anode.

In case of a high temperature fuel cell operating at a temperature of above 500°C, such as MCFC and SOFC, Ni is generally used as an electrode material. For example, in MCFC, porous Ni is used as an anode and NiO (oxidized Ni) is used as a cathode. Also, in SOFC, a cermet in which Ni is mixed with electrolytic material such as zirconia or ceria and the like is used as an anode.

A serious problem in the anode where an oxidation reaction of fuel is generated is

that, under an operating condition of high temperature and heavy load of above $2kg/cm^2$, a sintering and a creep are caused so that porosity is reduced and a micro-structural deformation such as shrinkage is generated, degrading performance thereof.

That is to say, Ni electrode adapted to high temperature fuel cell is manufactured to have porous structure in order to enlarge reactive area of the electrode and to provide a gas passage way, but, if Ni electrode is used at a high temperature for a long time, it has defects in that surface area and reaction rate thereof are reduced. Also, if a fuel cell stack many sheets of unit cells are laminated one after another is operated for a long time, a creep is caused in the porous Ni electrode by a load of the fuel cell, causing a defect of performance reduction.

To solve this problem, there has been proposed a method for improving resistance to sintering and a creep of the nickel electrode, wherein 10wt% Cr is added to Ni to form an intermetallic compound between Ni and Cr, or oxides such as Cr_2O_3, $LiCrO_2$ and so forth are formed on the surface of nickel electrode.

It has been reported that the modulus of strain of conventional Ni-10%Cr anode by creep is below 5%, but $LiCrO_2$ formed on the surface is dissolved in the electrolyte to weaken resistance to sintering and creep when operated long time. As a result, in order to improve a feature of creep, after the middle of 1980s, there have been studied a method of oxide dispersion strengthened (ODS) in which metal oxide including alumina is dispersed over the Ni electrode, and other methods using Ni-Al or Ni-Cr alloy as an anode, the alloy containing small quantities of Al or Cr that is preferentially oxidized relative to Ni.

ODS method had an effect in improvement of creep feature, but also had a limit in manufacturing an electrode having proper mechanical strength and electric conductivity.

Meanwhile, the method using an alloy electrode is a method which has the same concept as the ODS method and which is proposed to solve the problem in degradation of mechanical strength by previously dispersing Al or Cr, which will be oxidized during a

manufacturing process of an electrode or during an operation, over the Ni substrate so that the produced oxides distribute over inside and outside of the substrate and the surface thereof. Known as best material among the alloy electrodes is Ni-Al alloy electrode, which has below 0.5% of the creep strain rate so that, even in $1m^2$, the size of commercial electrode, an increase of contact resistance is very slight.

However, Ni-Al alloy electrode has problems in that its price is higher than the existing material and in that it is not easily sintered by a conventional manufacturing process of electrode.

Accordingly, it has been required a method for manufacturing a new alloy anode for electrode of fuel cells, which is easy to be sintered and manufactured at low cost, providing a simple and economical process, and which has excellent working property advantageous for scale-up and mass production.

SUMMARY OF THE INVENTION

Accordingly, the present invention has been made to solve the above-mentioned problems occurring in the prior art, and an object of the present invention is to provide to a method for manufacturing Ni-Al alloy anode for fuel cells, in which, using nickel powders, Ni powders are mixed with Ni-Al alloy powders, which are hardly sintered in themselves, to assist a sintering of Ni-Al alloy, whereby Ni-Al alloy anode can be manufactured simply, economically and compatibly with mass production even by a conventional manufacturing process for an electrode.

Another object of the present invention is to provide Ni-Al alloy anode for fuel cells, which are manufactured by the method so that structural stability thereof is excellent while maintaining reactive activity thereof as it is.

In order to accomplish the above object, there is provided a method for manufacturing Ni-Al alloy anode for fuel cells using nickel powders, wherein the nickel powders are mixed as sintering aids into Ni-Al alloy powders.

According to the method for manufacturing Ni-Al alloy anode for fuel cells using nickel powders, mixing ratio of Ni-Al alloy powders to Ni powders is 30:70 to 70:30.

According to the method for manufacturing Ni-Al alloy anode for fuel cells using nickel powders, mixing ratio of Ni-Al alloy powders to Ni powders is 40:60 to 60:40.

Ni-Al alloy anode for fuel cells of the present invention is manufactured by the method described above.

BRIEF DESCRIPTION OF THE DRAWINGS

The above and other objects, features and advantages of the present invention will be more apparent from the following detailed description taken in conjunction with the accompanying drawings, in which:

FIG. 1 is a schematic view showing a structure of Ni-Al alloy anode for fuel cells manufactured using nickel powders by the present invention; and

FIG. 2 is a graphical representation showing performance of unit electrode using Ni-Al alloy anode for fuel cells manufactured using nickel powders by the present invention.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

Hereinafter, a preferred embodiment of the present invention will be described with reference to the accompanying drawings.

Since it is difficult for Ni-Al alloy powders to be sintered at high temperature, mass

production of Ni-Al alloy anode is very difficult.

The manufacturing method of Ni-Al anode according to the present invention is a method in which Ni powders are mixed to facilitate a sintering of Ni-Al alloy anode. Herein, Ni powders should be added by certain quantity to the extent that they assist only sintering of Ni-Al alloy powders. To maintain features of the existing Ni-Al alloy anode as it is, a microstructure of the anode should be controlled as to have a microstructure as shown in FIG. 1.

That is, a feature resistant to a creep the existing Ni-Al alloy anode has can be expected only when Ni-Al alloy powders have a microstructure with 3-D network as shown in FIG. 1.

In the present invention, a resistant feature to the creep is changed according to a volume ratio (mass ratio) of Ni-Al alloy powders to added Ni powders. Beyond a specific volume ratio that Ni-Al alloy powders form a structure of 3-D network, the resistant feature to creep becomes to abruptly increase.

The microstructure of the anode is determined in consideration of the securing of reaction area and gas transfer passage way, distribution in MCFC and electric conductivity, so that a thickness of about 0.8mm, an initial porosity of above 50%, an average pore size of 3~5 μm are typically provided. The anode with such structure is generally manufactured by a tape casting method, which is advantageous for scale-up. Since Ni-Al alloy anode for fuel cells can be manufactured by a conventional method, the detailed explanation of the method will be omitted.

Hereinafter, a construction and an effect thereby of the present invention will be described in detail with reference to the following embodiment. Although the following embodiment illustrates contents of the present invention, the present invention should not be

limited to the embodiment.

Embodiment 1

In this embodiment, Ni-Al alloy anode is manufactured by the following method.

Ni-Al alloy powders and Ni powders were mixed with each other in a volume ratio of 50:50, and then sintered at 1000°C for more than 3 hours. The porosity and pore size of the electrode were proved to be similar to those of the existing Ni-Cr anode.

The manufactured anode was adapted to the unit cell and operated at 650°C.

FIG. 2 shows a result of measuring performance of the unit cell to which the anode is adapted, the anode being manufactured by mixing Ni-Al alloy powders and Ni powders in a volume ratio of 50:50. The unit cell according to the present invention maintains a performance of above 0.8V at a load of $150mA/cm^2$ without the degradation of performance for more than 3000 hours. However, near on 3300 hours, the measuring of cell performance was stopped while the temperature was raised by about 800°C due to a disorder of thermocouple.

Generally, performance degradation of cell caused by a structural instability of the anode involves an increase of internal resistance (IR). However, as shown in FIG. 2, the anode manufactured by the present invention maintains value of IR as it is, which indicates that the anode of the present invention has a structural stability superior to that of the existing anode.

As described above, the present invention provides a method for manufacturing Ni-Al alloy anode for fuel cells, in which, using nickel powders, Ni powders are mixed with Ni-Al alloy powders, which are hardly sintered in themselves, to assist a sintering of Ni-Al alloy,

whereby Ni-Al alloy anode can be manufactured simply, economically and compatibly with mass production even by a conventional manufacturing process for an electrode.

Also, the method for manufacturing Ni-Al alloy anode for fuel cells using nickel powders utilizes the existing manufacturing process of electrode based on Ni as it is, so that Ni-Al alloy anode can be manufactured economically and compatibly with scale-up of the anode.

Although preferred embodiments of the present invention have been described for illustrative purposes, those skilled in the art will appreciate that various modifications, additions and substitutions are possible, without departing from the scope and spirit of the invention as disclosed in the accompanying claims.